Indian J. Phys. **78(12)**, 1329-1333 (2004)

AN INTERNATIONAL JOURNAL
IJP

Ultrasonic study of intermolecular association through hydrogen bonding in aqueous solutions of D-mannitol

M Sethu Rama*[1] and G Amirthaganesan[2]

[1] Department of Physics, [2]Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641 020, Tamil Nadu, India

E-mail : sethu_muthu2003@yahoo.co.in

Received 30 April 2004, accepted 17 September 2004

Abstract : The density and ultrasonic velocity measurements were carried out in aqueous solutions of D-mannitol in the concentration range of 0.1–1.0 m between 303.15 K and 323.15 K with 5 K increments. Using the measured values of density (ρ) and ultrasonic velocity (u), other acoustical parameters such as adiabatic compressibility (β_{ad}), acoustic impedance (Z), hydration number (H_n) and intermolecular free length (L_f) were evaluated. These parameters were interpreted as due to the formation of intermolecular hydrogen bonding between the hydroxyl groups of D-mannitol and water molecules.

Keywords : Ultrasonic velocity measurement, acoustic impedance, hydrogen bonding, clusters.

PACS Nos. : 43.35.Bf, 33.15. Fm.

1. Introduction

Carbohydrates play an important role in animal and plant life. Understanding the behaviour of aqueous carbohydrate solutions is of utmost importance in biology, medicine and in understanding the taste quality exhibited by them [1]. In the last decades, the study of carbohydrates/ saccharides has become a subject of increasing interest because of the multidimensional physical, biochemical and industrially useful properties of these compounds [2–5]. In pharmaceutical and chemical industries, the simple saccharides have received considerable attention for their ability to protect biological macromolecules [6,7]. Sugars and polyols are well known stabilizing agents in their native state for proteins and enzymes because of their ability to 'enhance' the structure of water [8,9]. Various thermodynamic [10–12] and spectroscopic [13–15] studies have shown that the hydration of saccharides depends upon the number of hydroxyl groups.

Apparent molar volumes and apparent specific volumes reflect the state of hydration of the molecules and thus their extent of interaction with water structure [1]. The range of apparent specific volumes reported are 0.13–0.49 cm^3/g for salty molecules, 0.55–0.68 cm^3/g for sweet molecules, 0.53–0.88 cm^3/g for sweet bitter molecules and a much wider range 0.16–0.85 cm^3/g for sour molecules. Compressibility hydration numbers are also determinable from the measurement of adiabatic compressibilities and these reflect the number of water molecules that surround the solute molecules. In this paper, an attempt has been made to understand the molecular interaction of mannitol with water by evaluating various acoustic parameters based on the ultrasonic velocity measurements in aqueous solutions of mannitol at different concentrations and temperatures.

2. Experimental

Aqueous solutions of D-mannitol (AR grade) in the concentration range of 0.1–1.0 m are prepared by dissolving known amounts of mannitol in the double distilled water. Ultrasonic velocities for the solutions were measured using M-81 model, 2 MHz ultrasonic

*Corresponding Author

interferometer (Mittel Enterprises, New Delhi) with a reproducibility of ±0.4 m/sec at 25°C. The temperature was constantly maintained by circulating water from a thermostatically controlled water bath with an accuracy of ±0.1°C. The density measurements were made by using a 50 ml specific gravity bottle and the accuracy of the measurements is ±0.0001 × 10^3 kg/m^3. An analytical balance was employed for mass measurements with an accuracy of ±0.0001 × 10^{-3} kg.

3. Theory

Using the measured data, the acoustical parameters such as adiabatic compressibility (β_{ad}), acoustic impedance (Z), hydration number (H_n) and intermolecular free length (L_f) were calculated using the following standard expressions.

Adiabatic compressibilities, β_{ad} (N^{-1} m^2), were calculated from both density and sound velocity values using the following equation.

$$\beta_{ad} = \frac{1}{u^2 \rho} \tag{1}$$

where

u = sound velocity of solution (m/sec) and

ρ = density of the solution at the same temperature (kg/m^3).

The values of acoustic impedance, Z (kg m^{-2} s^{-1}), and hydration number, H_n were calculated from density, sound velocity data and the computed values of adiabatic compressibilities by using eqs. (2) and (3) respectively.

$$Z = \rho u, \tag{2}$$

$$H_n = 1 - \frac{\beta_{ad}}{\beta_{ab}^0} \tag{3}$$

where n_w = number of moles of water (mol/kg),

n_s = number of moles of solute (mol/kg) and

β_{ad}^0 = adiabatic compressibility of water at a particular temperature (N^{-1} m^2).

Intermolecular free lengths L_f(Å) are calculated from the following expression.

$$L_f = K_T (\beta_{ad})^{1/2}, \tag{4}$$

where K_T = temperature dependent constant,

$$= (193.875 + 0.0375\ T) \times 10^{-8},$$

T is the absolute temperature [16].

4. Results

The measured and other calculated parameters *viz.*, density, ultrasonic velocity, adiabatic compressibility, acoustic impedance, hydration number and intermolecular free length for aqueous mannitol solutions are presented in Table 1. The plots of ultrasonic velocities and adiabatic compressibilities as a function of temperature are depicted in Figures 1 and 2 respectively.

5. Discussion

5.1. Ultrasonic velocity (u) :

It can be observed from Figure 1 that the ultrasonic velocity is found to increase with the increase in mannitol concentration. The increase in ultrasonic velocity in any solution indicates the maximum association among the molecules of a solution. The maximum association is due to the hydrogen bonding between the solute and solvent molecules. The conductivity studies of sucrose solutions [17] and acoustical properties of fructose and maltose in water and in aqueous NH_4Cl solutions [18] also confirm the formations of hydrogen bonds between the solute and water molecules. In the present study, we observe a steady increase in ultrasonic velocity as concentration increases. This is due to the maximum possible association in aqueous mannitol solutions because of the presence of six-OH groups in a mannitol molecule.

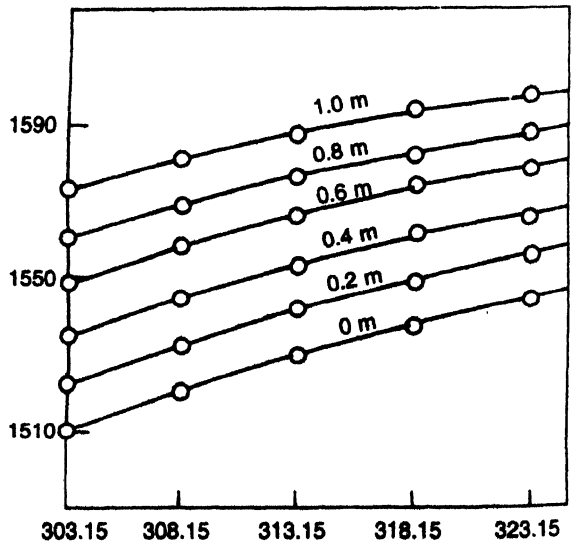

Figure 1. Variation of ultrasonic velocity with respect to temperature in aqueous solutions of D-mannitol.

The ultrasonic velocity of mannitol solutions are found to increase with increasing temperature. This behaviour is similar to that of pure water, where the ultrasonic velocity increases with increase in temperature. As the temperature increases, the hydrogen bonds among water molecules

break and more monomeric water molecules are formed. These broken water molecules enter the vacant spaces present in the cage-like water structures and thus get 'trapped'. As a result, the number of close-packed water structure increases with the increase in temperature. This increase in close-packed water structures forms the material medium for the propagation of ultrasonic waves. Thus, the ultrasonic velocity increases with the increase in temperature for pure water as well as for aqueous mannitol solutions in any given concentration. In addition, in mannitol solutions, the polar mannitol molecules form more compact structures with the solvent water molecules through hydrogen bonding. This effect favours a decrease in compressibility. With increase in temperature, however, the mean distance between the molecules tends to increase with a corresponding increase in compressibility. These two opposing tendencies result in a net decrease in compressibility and hence an increase in ultrasonic velocity [eq. (1)]. As observed in Table 1, the ultrasonic velocity for the mannitol solutions increases with the increase in temperature in all the concentrations.

5.2. *Adiabatic compressibility* (β_{ad}) :

When an ion is added to a solvent, it attracts certain solvent molecules towards itself by wrenching the molecule from bulk of the solvent due to the force of electrostriction. Because of this, the available solvent molecule for the next incoming ion gets decreased. This process is called the compression. Every solvent has a limit for the compression called the limiting compressibility value. The compressibility of a solvent is higher than that of a solution and it decreases with the increase in concentration of the solution. With increase in ionic solute concentration, their electrostrictive forces cause the water structure to break and the solute surrounded water molecules are more compactly packed. This hydration effect in turn, results in reducing the compressibility with increasing ionic solute concentration. In the aqueous mannitol solutions, it is observed

(Figure 2 and Table 1) that adiabatic compressibilities decrease with the increase in temperature and mannitol concentrations. This confirms the presence of solute-solvent interactions through dipole-dipole interactions of the-OH groups of mannitol with the surrounding water molecules [18].

5.3 *Acoustic impedance (Z)* :

It is observed from Table 1 that the values of acoustic impedance vary linearly with the increase in mannitol concentrations. The linear variation of acoustic impedance with concentration confirms the presence of molecular association between the solute-solvent molecules.

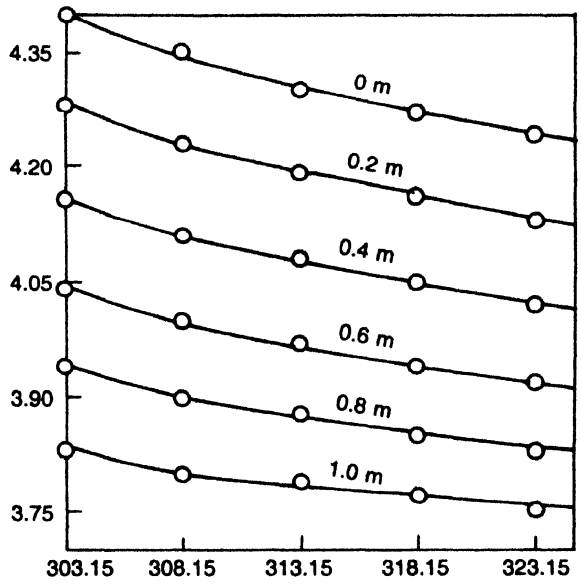

Figure 2. Variation of adiabatic compressibility with respect to temperature in aqueous solutions of D-mannitol.

5.4. *Hydration number* (H_n) :

The hydration of solute molecules in water is explained on the basis of Frank and Wen [19] model of solute-solvent interaction, which pictures three different solvent structure regions in the neighbourhood of the solute. Just out side the molecule, there is a layer of immobilized and compressed water as a result of electrostrictive and other attractive forces exerted the solute. This layer is surrounded by a slightly less compressed or 'structure-broken' region of water molecules, distantly affected by these forces. The outer most layer is bulk water which possesses the typical tetra-coordinated hydrogen-bonded structure not affected by any of the above forces. Compressibility measurements indicate the changes in the first two layers of solvent around the solute molecule. In the case of carbohydrate molecules, the water structure is slightly disturbed by the hydrogen-bonded network around the solute; this holds the water around the solute firmly, making the hydration layer even less compressible. From the computed values of H_n, it is found that in all the concentrations, each mannitol molecule is closely bound and forms a complex in a cluster organization with a fixed number of water molecules.

5.5. *Intermolecular free length* (L_f) :

Intermolecular free length shows a similar behaviour as reflected by the compressibility values. The decreased

Table 1. Ultrasonic velocity and other acoustical parameters for aqueous mannitol solutions.

T K	C molal (mol/kg)	$\rho \times 10^3$ kgm^{-3}	u m s^{-1}	$\beta_{ad} \times 10^{-10}$ N^{-1} m^2	$Z \times 10^5$ kgm^{-2}s^{-1}	H_n	L_f Å
303.15	0	0.9956	1510.4	4.40	15.038	0	0.4354
	0.1	1.0018	1516.8	4.33	15.196	8.0	0.4322
	0.2	1.0066	1522.4	4.28	15.325	7.3	0.4296
	0.3	1.0137	1528.4	4.22	15.494	7.5	0.4264
	0.4	1.0193	1535.2	4.16	15.649	7.5	0.4233
	0.5	1.0260	1544.0	4.08	15.842	7.9	0.4195
	0.6	1.0309	1548.0	4.04	15.958	7.4	0.4175
	0.7	1.0372	1554.8	3.98	16.023	7.4	0.4144
	0.8	1.0424	1560.0	3.94	16.262	7.2	0.4120
	0.9	1.0478	1565.0	3.89	16.405	7.1	0.4094
	1.0	1.0529	1572.8	3.83	16.561	7.1	0.4066
308.15	0	0.9940	1520.0	4.35	15.109	0	0.4369
	0.1	1.0001	1527.6	4.28	15.277	8.8	0.4334
	0.2	1.0049	1532.4	4.23	15.399	7.4	0.4310
	0.3	1.0121	1538.4	4.17	15.570	7.6	0.4278
	0.4	1.0176	1544.4	4.11	15.717	7.4	0.4250
	0.5	1.0238	1551.6	4.05	15.886	7.5	0.4217
	0.6	1.0291	1557.2	4.00	16.025	7.3	0.4191
	0.7	1.0351	1564.8	3.94	16.198	7.4	0.4159
	0.8	1.0406	1568.8	3.90	16.326	7.1	0.4137
	0.9	1.0459	1573.6	3.86	16.458	6.9	0.4114
	1.0	1.0509	1580.4	3.80	16.608	6.9	0.4087
313.15	0	0.9922	1529.2	4.30	15.173	0	0.4386
	0.1	0.9981	1536.4	4.24	15.335	8.4	0.4352
	0.2	1.0028	1541.2	4.19	15.456	7.2	0.4328
	0.3	1.0101	1547.2	4.13	15.629	7.5	0.4295
	0.4	1.0155	1552.8	4.08	15.768	7.2	0.4269
	0.5	1.0218	1559.2	4.02	15.932	7.3	0.4238
	0.6	1.0269	1565.2	3.97	16.074	7.2	0.4212
	0.7	1.0329	1570.0	3.92	16.217	7.0	0.4187
	0.8	1.0383	1575.2	3.88	16.356	6.9	0.4162
	0.9	1.0433	1579.6	3.84	16.480	6.7	0.4140
	1.0	1.0486	1586.0	3.79	16.631	6.6	0.4113
318.15	0	0.9902	1537.6	4.27	15.225	0	0.4405
	0.1	0.9959	1545.2	4.20	15.389	8.6	0.4370
	0.2	1.0010	1548.0	4.16	15.496	6.6	0.4352
	0.3	1.0077	1553.2	4.11	15.651	6.8	0.4323
	0.4	1.0137	1558.8	4.05	15.802	6.8	0.4294
	0.5	1.0194	1566.4	3.99	15.969	–	0.4261
	0.6	1.0249	1573.6	3.94	16.128	–	0.4231
	0.7	1.0308	1577.2	3.89	16.259	6.9	0.4209
	0.8	1.0363	1581.6	3.85	16.422	6.7	0.4186
	0.9	1.0412	1586.8	3.81	16.555	6.6	0.4162
	1.0	1.0465	1592.8	3.76	16.669	6.5	0.4136
323.15	0	0.9880	1544.8	4.24	15.263	0	0.4428
	0.1	0.9951	1551.2	4.20	15.389	8.4	0.4394
	0.2	0.9997	1555.2	4.16	15.496	6.9	0.4372
	0.3	1.0068	1559.6	4.11	15.651	6.8	0.4345
	0.4	1.0125	1565.6	4.05	15.802	6.9	0.4316
	0.5	1.0187	1572.0	3.99	15.969	–	0.4285
	0.6	1.0235	1577.6	3.94	16.128	6.8	0.4260
	0.7	1.0299	1582.4	3.89	16.259	6.8	0.4234
	0.8	1.0349	1587.2	3.85	16.422	6.6	0.4211
	0.9	1.0402	1590.0	3.81	16.555	6.3	0.4193
	1.0	1.0455	1596.0	3.76	16.669	6.3	0.4166

compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length as observed in Table 1. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free lengths after mixing the components suggested by Eyring and Kincaid [20], the ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing the components. In the present investigation, it has been observed that the intermolecular free lengths decrease on increasing the concentration of mannitol. This behaviour indicates significant interaction between the solute and solvent molecules suggesting a structure promoting tendency of the added mannitol [18].

6. Conclusions

In this paper, a systematic study of D-mannitol in water has been carried out at different concentrations and at different temperatures. The experimental ultrasonic velocity data and other acoustical parameters contain valuable information regarding the solute-solvent interactions in the aqueous solutions. There is a uniform decrease in the density and increase in the intermolecular free length with the increase in temperature indicating loosening of intermolecular forces due to thermal agitation of the molecules in the aqueous mannitol solutions at high temperatures. It may be concluded that the ultrasonic studies provide a comprehensive investigation of molecular association between mannitol and water molecules arising due to the hydrogen bonding. The calculated values of intermolecular free lengths with increasing mannitol concentrations also strongly support the association between D-mannitol and water molecules. These conclusions give scope for further studies on the thermodynamic properties for the system.

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